Supporting Information:

Electrocatalytic Hydrogen Evolution at Low Overpotentials by Cobalt Macrocyclic Glyoxime and Tetra-Imine Complexes

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General Parameters for Simulation

Scan Rate	Cycles	Ru(Ohm)	CdI(F)	Temp.(K)	Geometry	Area(cm^2)
0.1 V/s	1	0	0	298.2	Planar	0.07

Diffusion	Potential Steps (V)	Gauss-Newton Iteration	Noise Level (A)
Semi-Infinite 1D	0.005	2	0

Space perpendicular to electrode:

Grid Expansion Factor	Rel. Truncation Error	Xmas/SQRT(Dt)
0.5	0.0001	6

Local FEM error level: 0.05

Steady State analysis of the bimetallic pathway

We have written the kinetic equations for the bimetallic pathway as:

$$\text{Co(I)} + \text{HA} \rightarrow \text{Co(III)-H} + \text{A}^- \quad K_4, k_4 \tag{4}$$

$$\text{Co(III)-H} + \text{Co(III)-H} \rightarrow 2\ \text{Co(II)} + \text{H}_2 \quad K_7, k_7 \tag{7}$$

$$\frac{d[\text{Co(III)-H}]}{dt} = k_4[\text{Co(I)}][\text{HA}] - k_{-4}[\text{Co(III)-H}][\text{A}] - 2k_7[\text{Co(III)-H}]^2$$

$$\frac{d[\text{Co(II)}]}{dt} = 2k_7[\text{Co(III)-H}]^2 = 2\frac{d[\text{H}_2]}{dt}$$

Assuming a steady state for Co(III)-H

$$2k_7[\text{Co(III)-H}]^2 + k_{-4}[\text{Co(III)-H}][\text{HA}] - k_4[\text{Co(I)}][\text{HA}] = 0$$

solving we obtain,

$$[\text{Co(III)-H}] = \frac{-k_{-4}[A] \pm \sqrt{(k_{-4}[\text{A}])^2 + 8k_7k_4[\text{Co(I)}][\text{HA}]}}{2k_7}$$

If the first term in the square root is larger then second, $(k_{-4}[\text{A}])^2 >> 8k_7k_4[\text{Co(I)}][\text{HA}]$, then,

$$[\text{Co(III)-H}] = \frac{-k_{-4}[\text{A}] + k_{-4}[\text{A}]\sqrt{1 + \frac{8k_7k_4[\text{Co(I)}][\text{HA}]}{(k_{-4}[\text{A}])^2}}}{4k_7}$$

$$\approx \frac{-k_{-4}[\text{A}] + k_{-4}[\text{A}] + \frac{1}{2}\frac{8k_{-4}k_7k_4[\text{Co(I)}][\text{HA}]}{(k_{-4}[\text{A}])^2}}{4k_7}$$

$$[\text{Co(III)-H}] \approx \frac{1}{2}\frac{8k_7k_4[\text{Co(I)}][\text{HA}]}{4k_7k_{-4}[\text{A}]}$$

$$= \frac{k_4[\text{Co(I)}][\text{HA}]}{k_{-4}[\text{A}]}$$

$$= K_4\frac{[\text{Co(I)}][\text{HA}]}{[\text{A}]}$$

$$\frac{d[\text{H}_2]}{dt} = k_7{K_4}^2\frac{[\text{CoI}]^2[\text{HA}]^2}{[\text{A}]^2}$$

The rate is second order in [Co(I)] and [HA] and inverse in $[\text{A}]^2$ with a rate constant as the product of the equilibrium constant for the rapid formation of the precursor hydride and the rate constant of the slow hydrogen formation reaction.

If second term is larger, $(k_{-4}[\text{A}])^2 << 8k_7k_4[\text{Co(I)}][\text{HA}]$, then:

$$[\text{Co(III)-H}] = \frac{-k_{-4}[\text{A}] + \sqrt{8k_7k_4[\text{Co(I)}][\text{HA}]}\sqrt{1 + \frac{(k_{-4}[\text{A}])^2}{4k_7k_4[\text{Co(I)}][\text{HA}]}}}{4k_7}$$

$$\approx \frac{\sqrt{8k_7k_4[\mathrm{Co(I)}][\mathrm{HA}]} - k_{-4}[\mathrm{A}]}{4k_7}$$

$$= \sqrt{\frac{k_4[\mathrm{Co(I)}][\mathrm{HA}]}{2k_7}}$$

$$\frac{d[\mathrm{H_2}]}{dt} = k_7\left(\sqrt{\frac{k_4[\mathrm{Co(I)}][\mathrm{HA}]}{2k_7}}\right)^2$$

$$= k_4[\mathrm{Co(I)}][\mathrm{HA}]$$

The rate is first order in [Co(I)] and [HA] with a rate constant of the show hydride formation reaction.

Electrocatalysis of 4a in the presence of HBF_4•Et_2O.

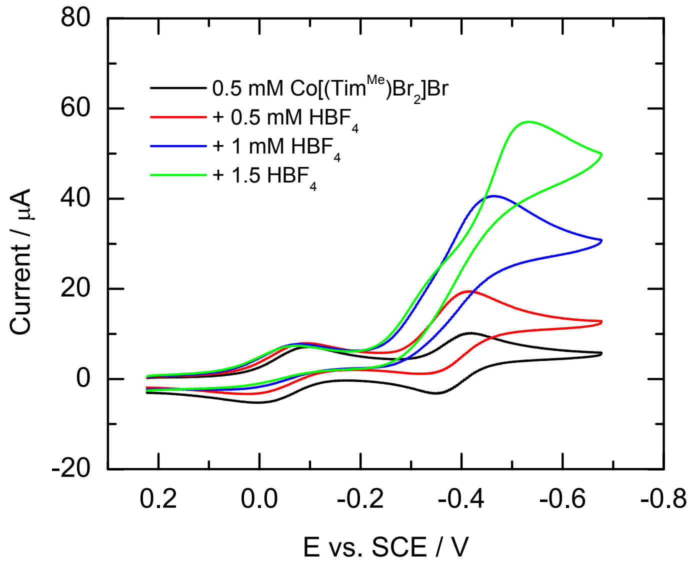
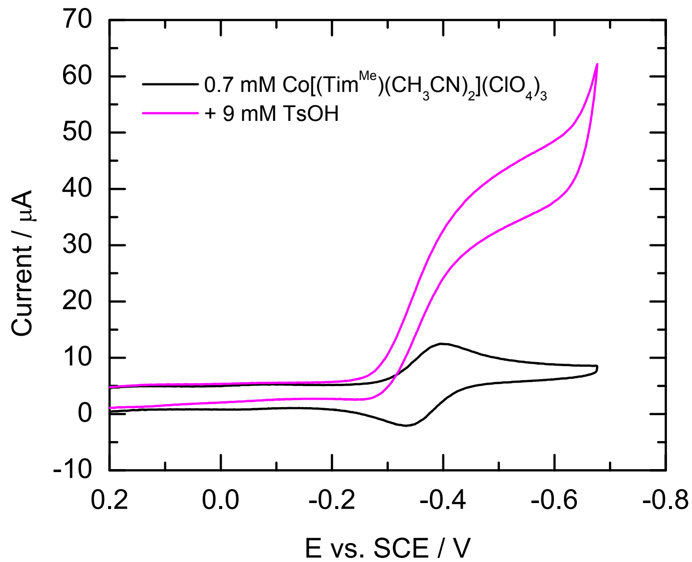


Figure S1. Cyclic voltammogram of **4a** in the presence of HBF_4•Et_2O recorded in an acetonitrile solution containing 0.1 M [$^nBu_4$][ClO_4]. Scan rate: 100 mV/s.

Electrocatalysis of 4b in the presence of TsOH•H_2O or HBF_4•Et_2O.



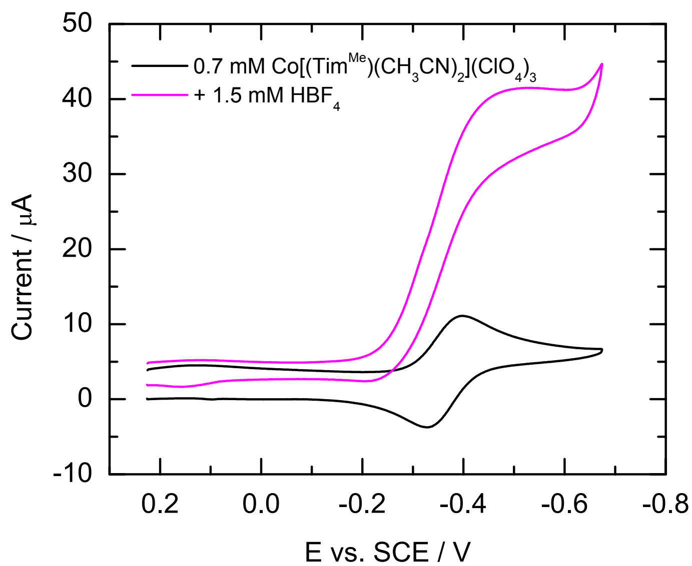


Figure S2. Cyclic voltammogram of **4b** in the presence of TsOH•H_2O (top) or HBF_4•Et_2O (bottom) recorded in an acetonitrile solution containing 0.1 M [$^nBu_4$][ClO_4]. Scan rate: 100 mV/s.

Electrocatalysis of 5a–b in the presence of HBF_4•Et_2O.

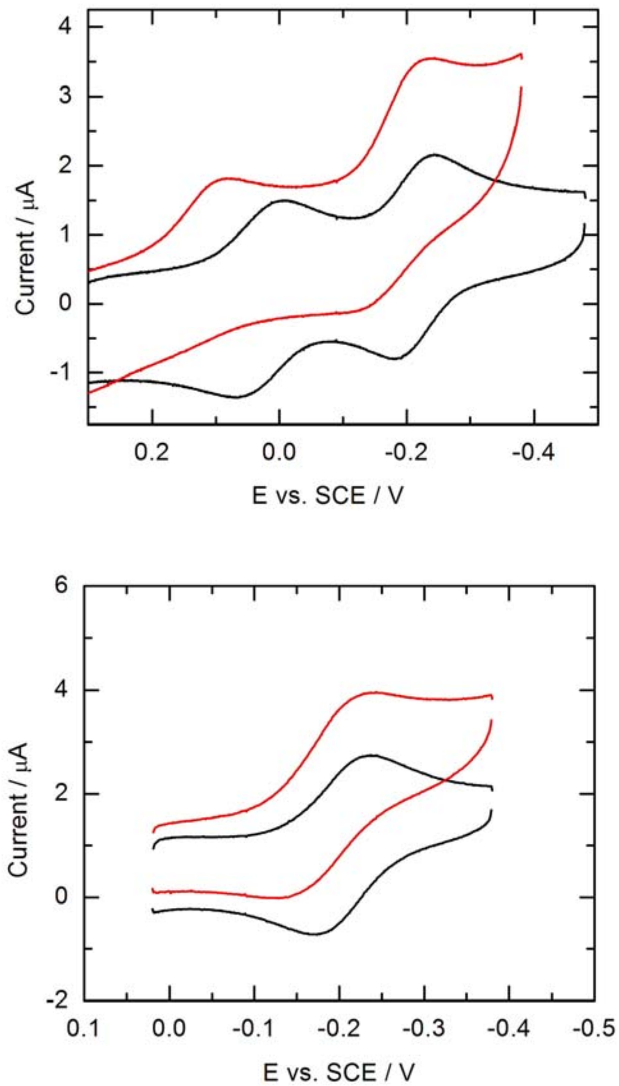
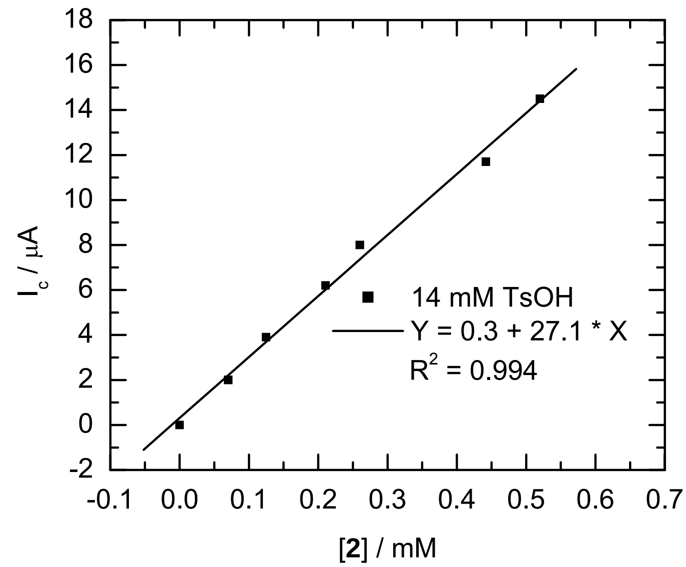


Figure S3. (Top): Cyclic voltammogram of 0.1 mM **5a** in CH_3CN solution containing 0.1 M [$^nBu_4N$][ClO_4] in the absence (black) and presence (red) of 1.5 mM HBF_4•Et_2O. (Bottom): Cyclic voltammogram of 0.15 mM **5b** in CH_3CN solution containing 0.1 M [$^nBu_4N$][ClO_4] in the absence (black) and presence (red) of 1.5 mM HBF_4•Et_2O. Scan rate: 100 mV /s^{-1}; Glassy carbon electrode. The reaction for the shift in the $Co^{III/II}$ potential upon addition of acid is not clear at this point.



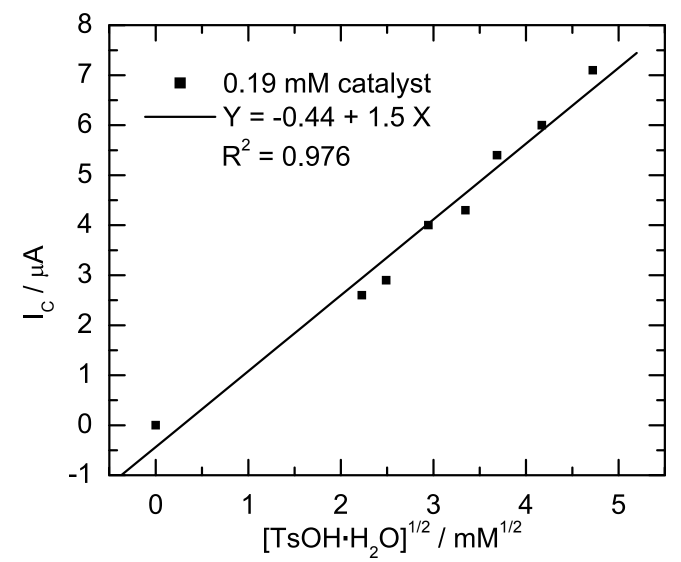
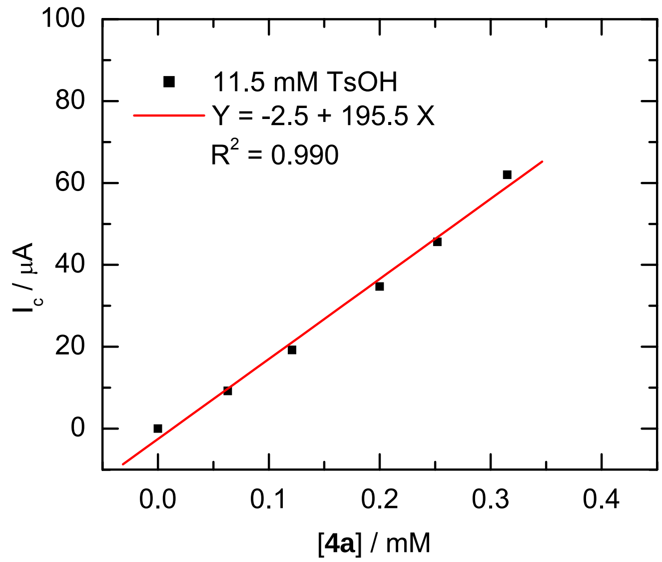


Figure S4. Dependence of the catalytic current i_c on the concentrations of catalyst and acid for complex **2**; TsOH•H_2O was used as the acid, with a scan rate of 100 mV/s.



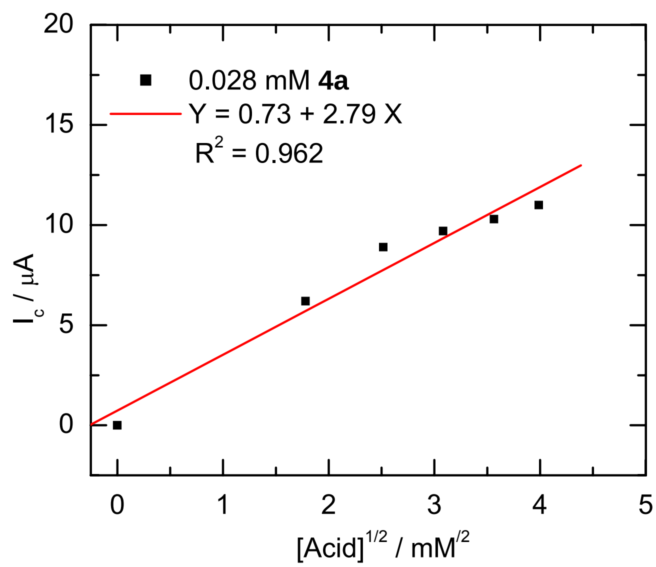
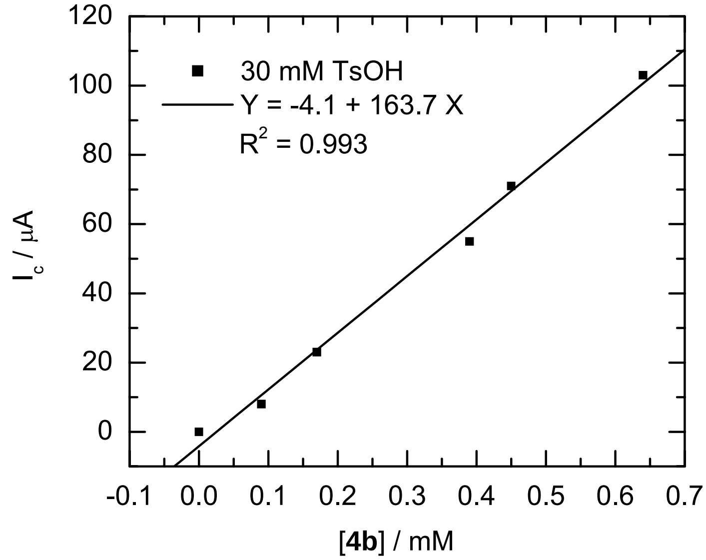


Figure S5. Dependence of the catalytic current i_c on the concentrations of catalyst and acid for complex **4a**; TsOH•H_2O was used as the acid.



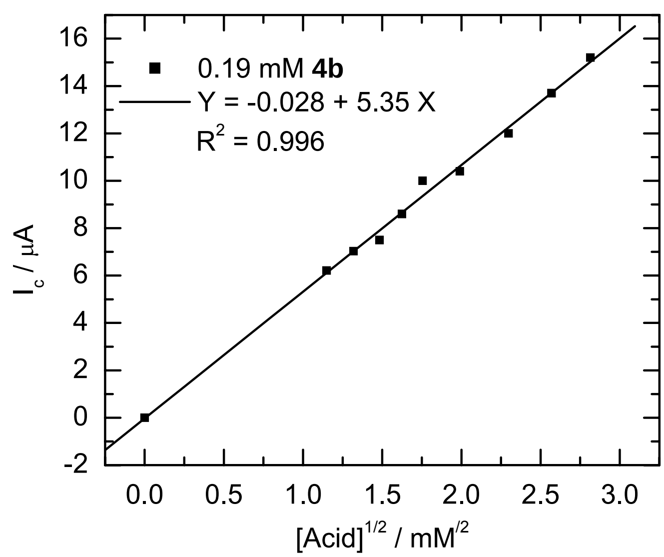
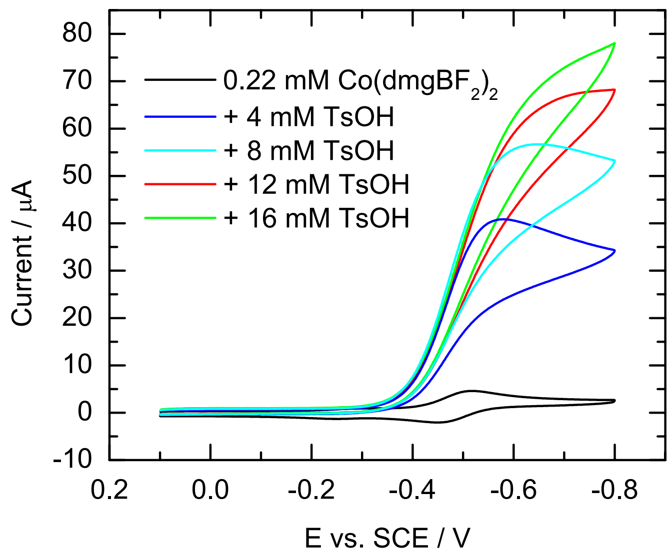
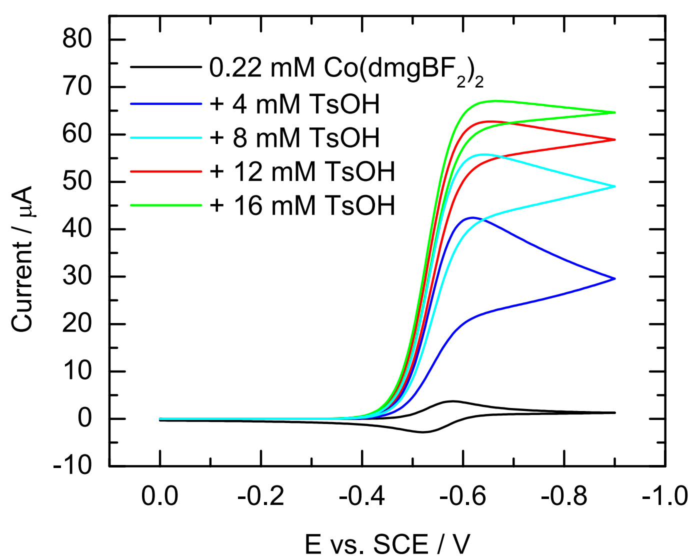


Figure S6. Dependence of the catalytic current i_c on the concentrations of catalyst and acid for complex **4b**; TsOH•H_2O was used as the acid.



0.22 mM Co(dmgBF2)2
+ 4 mM TsOH
+ 8 mM TsOH
+ 12 mM TsOH
+ 16 mM TsOH
Current / μA
E vs. SCE / V



0.22 mM Co(dmgBF2)2
+ 4 mM TsOH
+ 8 mM TsOH
+ 12 mM TsOH
+ 16 mM TsOH
Current / μA
E vs. SCE / V

Figure S7. Experimental and simulated spectra of the catalytic waves for H_2 evolution catalysis using 0.22 mM of **1** as the catalyst; top: experimental data; bottom: simulation using a bimetallic mechanism.

Specific Parameters for Simulation in Figure S7:

Estart (V)	Erev (V)	Eend (V)
0	-0.9	0

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + e^- → Co(II)	0.2	0.5	10000
Co(II) + e^- → Co(II)	-0.55	0.5	10000
H^+ + e^- → s	-0.23	0.5	0

Chemical reactions:

Rxn	Keq	kf	kb*
Co(I) + H^+ → Co-H	1e5	1.5e5	1.5
s + s → H_2	1	1e10	1e10
Co-H + Co-H → A + H_2	1	1.5e6	1.5e6
A → Co(II) + Co(II)	6.55*	1e10	1.53e9

* These constants are automatically calculated by the program

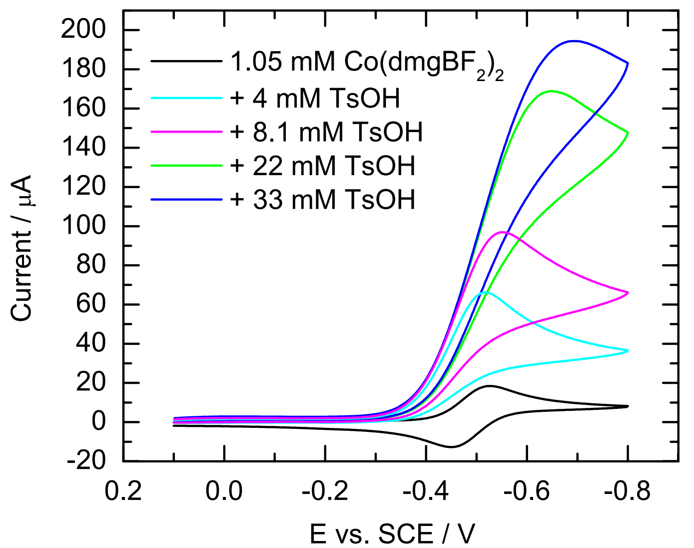
Species:

	D (cm^2/s)	C (M)		D (cm^2/s)	C (M)		D (cm^2/s)	C (M)

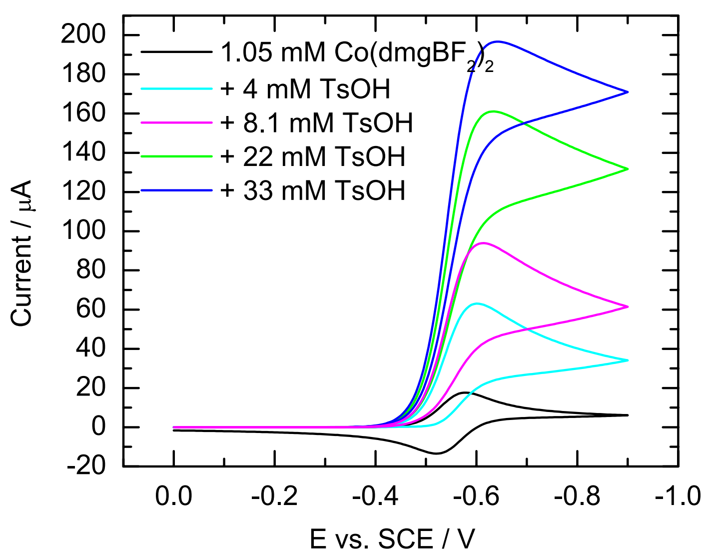
Co(III)	8e-6	0	Co-H	8e-6	0	A	8e-6	0
Co(II)	8e-6	2.2e-4	H_2	1e-5	0			
Co(I)	8e-6	0	s	1e-5	0			

Acid concentrations, H^+ represents TsOH

	D (cm^2/s)	C (M)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	0	4e-3	8e-3	12e-3	16e-3



1.05 mM Co(dmgBF$_2$)$_2$
+ 4 mM TsOH
+ 8.1 mM TsOH
+ 22 mM TsOH
+ 33 mM TsOH
Current / μA
E vs. SCE / V



1.05 mM Co(dmgBF$_2$)$_2$
+ 4 mM TsOH
+ 8.1 mM TsOH
+ 22 mM TsOH
+ 33 mM TsOH
Current / μA
E vs. SCE / V

Figure S8. Experimental and simulated spectra of the catalytic waves for H_2 evolution catalysis using 1.05 mM of **1** as the catalyst; top: experimental data; bottom: simulation using a bimetallic mechanism.

Specific Parameters for Simulation in Figure S8:

Estart (V)	Erev (V)	Eend (V)
0	-0.9	0

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + e^- → Co(II)	0.2	0.5	10000
Co(II) + e^- → Co(II)	-0.55	0.5	10000
H^+ + e^- → s	-0.23	0.5	0

Chemical reactions:

Rxn	Keq	kf	kb*
Co(I) + H^+ → Co-H	1e5	7000	0.07
s + s → H_2	1	1e10	1e10
Co-H + Co-H → A + H_2	1	9e5	9e5
A → Co(II) + Co(II)	6.55*	1e10	1.53e9

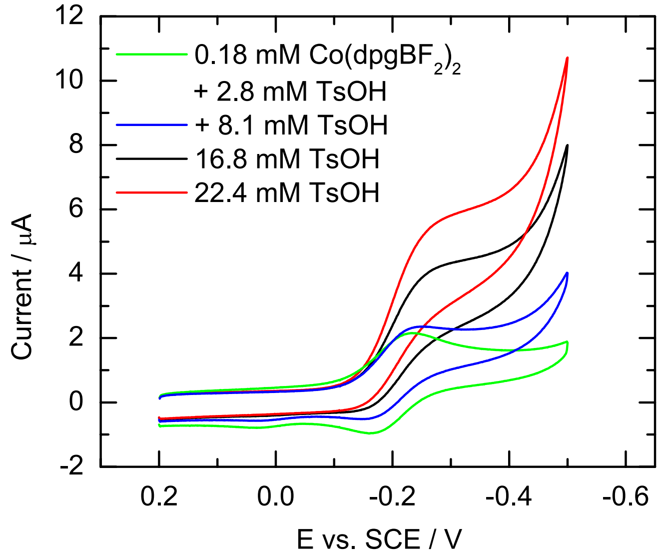
* These constants are automatically calculated by the program

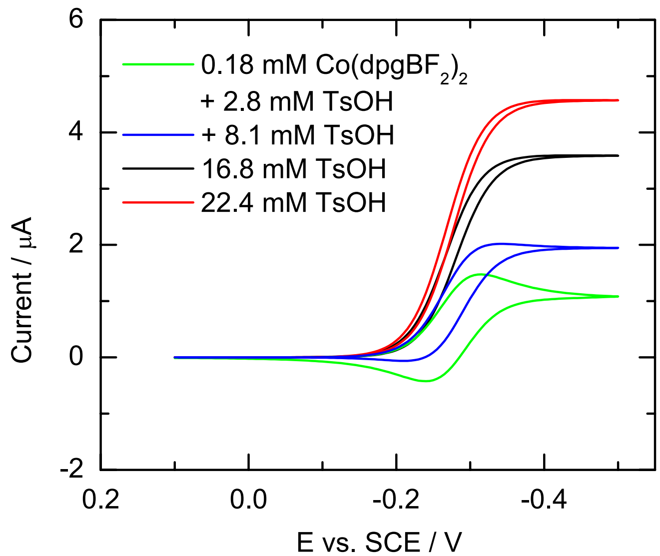
Species:

	D (cm^2/s)	C (M)		D (cm^2/s)	C (M)		D (cm^2/s)	C (M)
Co(III)	8e-6	0	Co-H	8e-6	0	A	8e-6	0
Co(II)	8e-6	1.05e-3	H_2	1e-5	0			
Co(I)	8e-6	0	s	1e-5	0			

Acid concentrations, H^+ represents TsOH

	D (cm^2/s)	C (M)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	0	4e-3	8.1e-3	22e-3	33e-3


0.18 mM Co(dpgBF$_2$)$_2$
+ 2.8 mM TsOH
+ 8.1 mM TsOH
16.8 mM TsOH
22.4 mM TsOH
Current / μA
E vs. SCE / V


0.18 mM Co(dpgBF$_2$)$_2$
+ 2.8 mM TsOH
+ 8.1 mM TsOH
16.8 mM TsOH
22.4 mM TsOH
Current / μA
E vs. SCE / V

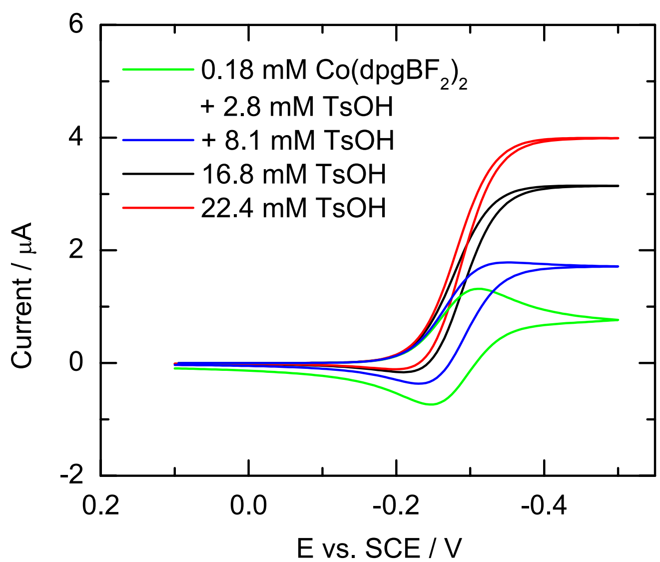

0.18 mM Co(dpgBF$_2$)$_2$
+ 2.8 mM TsOH
+ 8.1 mM TsOH
16.8 mM TsOH
22.4 mM TsOH
Current / μA
E vs. SCE / V

Figure S9. Experimental and simulated spectra of the catalytic waves for H_2 evolution catalysis using 0.18 mM of **2** as the catalyst; top: experimental data (the increase of current near E = -0.6 V is due to catalytic current at the Co(III)-H/Co(II)-H couple, see main text); middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, the simulations can not distinguish a monometallic mechanism from a bimetallic mechanism.

Specific Parameters for Simulation in Figure S9:

Estart (V)	Erev (V)	Eend (V)
0.1	-0.5	0.1

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + e^- → Co(II)	0.3	0.5	10000
Co(II) + e^- → Co(II)	-0.28	0.5	10000
H^+ + e^- → s	-0.23	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	Keq	kf	kb*
Co(I) + H^+ → Co-H	50	5000	100
s + s → H_2	1	1e10	1e10
Co-H + H^+ → Co(III) + H_2	1.54	800	518
Co(III) + Co(I) → Co(II) + Co(II)	6e9*	1e10	1.53

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
$Co(I) + H^+ \rightarrow Co\text{-}H$	10	4e4	4e3
$s + s \rightarrow H_2$	1	1e10	1e10
$Co\text{-}H + Co\text{-}H \rightarrow A + H_2$	4900*	1e6	204
$A \rightarrow Co(II) + Co(II)$	1e6	1e10	1e4

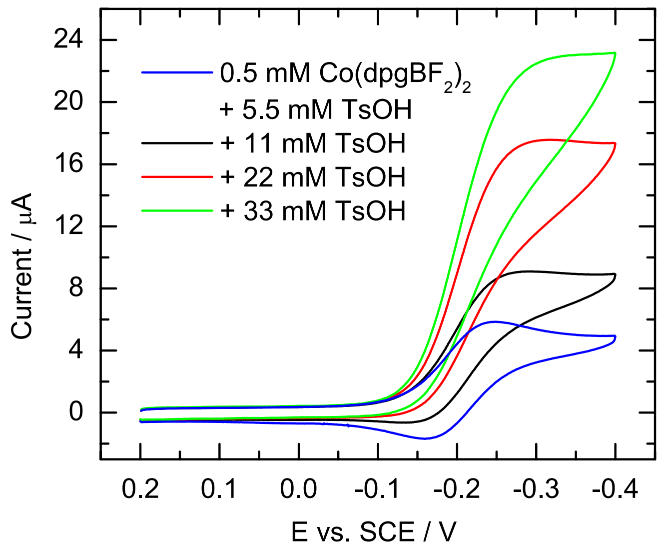
* These constants are automatically calculated by the program

Species:

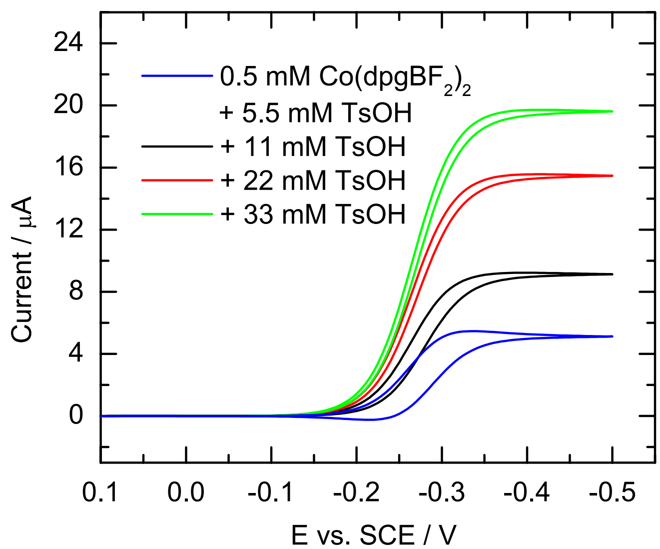
	D (cm^2/s)	C (M)		D (cm^2/s)	C (M)		D (cm^2/s)	C (M)
Co(III)	1.4e-6	0	Co-H	1.4e-6	0	A	1.4e-6	0
Co(II)	1.4e-6	1.8e-4	H_2	1e-5	0			
Co(I)	1.4e-6	0	s	1e-5	0			

Acid concentrations, H^+ represents TsOH

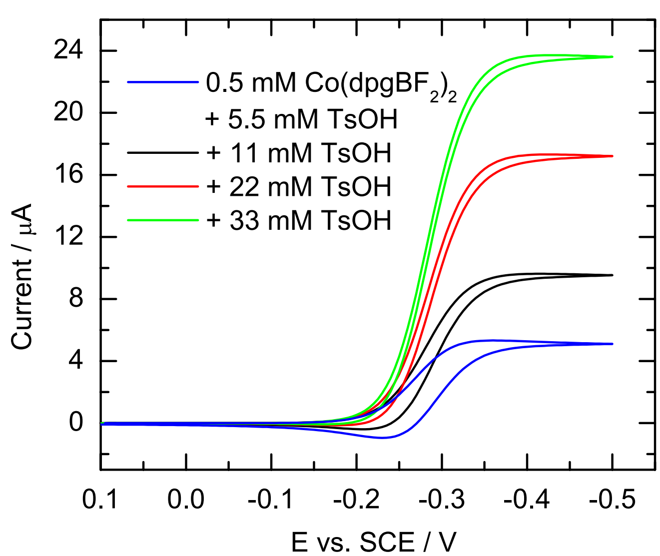
	D (cm^2/s)	C (M)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	0	2.8e-3	8.4e-3	16.8e-3	22.4e-3



0.5 mM Co(dpgBF2)2
+ 5.5 mM TsOH
+ 11 mM TsOH
+ 22 mM TsOH
+ 33 mM TsOH
Current / μA
E vs. SCE / V



0.5 mM Co(dpgBF2)2
+ 5.5 mM TsOH
+ 11 mM TsOH
+ 22 mM TsOH
+ 33 mM TsOH
Current / μA
E vs. SCE / V



0.5 mM Co(dpgBF2)2
+ 5.5 mM TsOH
+ 11 mM TsOH
+ 22 mM TsOH
+ 33 mM TsOH
Current / μA
E vs. SCE / V

Figure S10. Experimental and simulated spectra of the catalytic waves for H_2 evolution catalysis using 0.5 mM of **2** as the catalyst; top: experimental data; middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, the simulations can not distinguish a monometallic mechanism from a bimetallic mechanism.

Specific Parameters for Simulation in Figure S10:

Estart (V)	Erev (V)	Eend (V)
0.1	-0.5	0.1

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + e^- → Co(II)	0.3	0.5	10000
Co(II) + e^- → Co(II)	-0.28	0.5	10000
H^+ + e^- → s	-0.23	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	Keq	kf	kb*
Co(I) + H^+ → Co-H	50	5000	100
s + s → H_2	1	1e10	1e10
Co-H + H^+ → Co(III) + H_2	1.54	800	518
Co(III) + Co(I) → Co(II) + Co(II)	6e9*	1e10	1.53

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
$Co(I) + H^+ \rightarrow Co\text{-}H$	10	4e4	4e3
$s + s \rightarrow H_2$	1	1e10	1e10
$Co\text{-}H + Co\text{-}H \rightarrow A + H_2$	4900*	1e6	204
$A \rightarrow Co(II) + Co(II)$	1e6	1e10	1e4

* These constants are automatically calculated by the program

Species:

	D (cm^2/s)	C (M)		D (cm^2/s)	C (M)		D (cm^2/s)	C (M)
Co(III)	1.4e-6	0	Co-H	1.4e-6	0	A	1.4e-6	0
Co(II)	1.4e-6	5e-4	H_2	1e-5	0			
Co(I)	1.4e-6	0	s	1e-5	0			

Acid concentrations, H^+ represents TsOH

	D (cm^2/s)	C (M)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	0	5.5e-3	11e-3	22e-3	33e-3

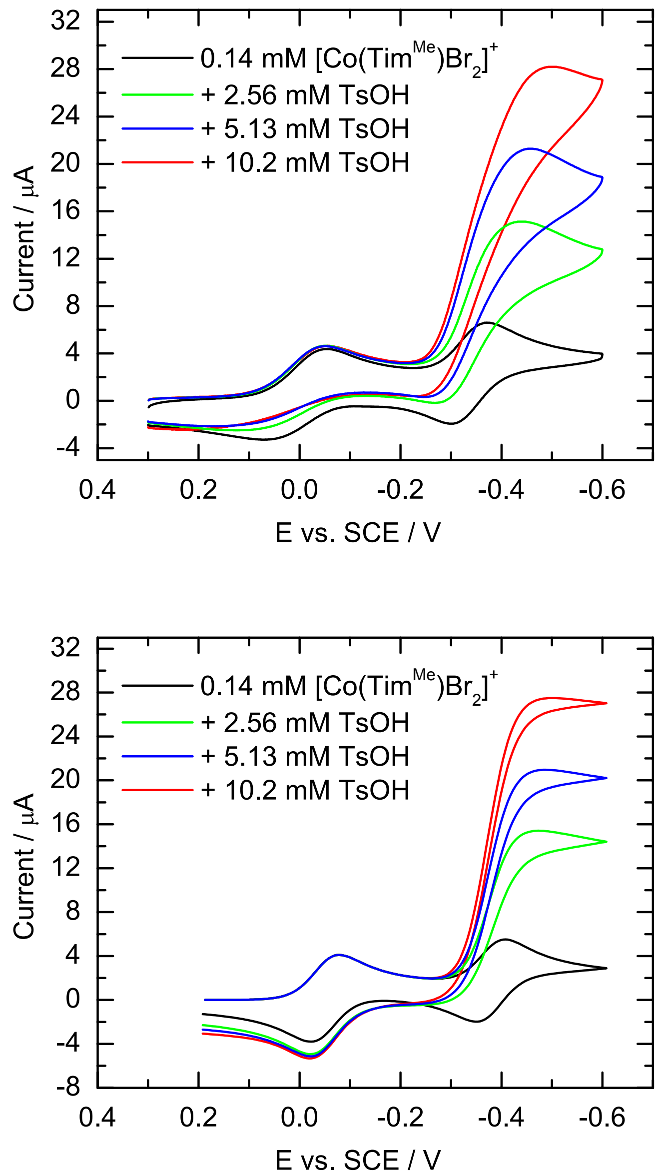


Figure S11. Experimental and simulated spectra of the catalytic waves for H_2 evolution catalysis using 0.14 mM of **4a** as the catalyst; top: experimental data; bottom: simulation using a bimetallic mechanism.

Specific Parameters for Simulation in Figure S11:

Estart (V)	Erev (V)	Eend (V)
0.2	-0.6	0.2

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + e^- → Co(II)	-0.05	0.5	10000
Co(II) + e^- → Co(II)	-0.38	0.5	10000
H^+ + e^- → s	-0.23	0.5	0

Chemical reactions:

Rxn	Keq	kf	kb*
Co(I) + H^+ → Co-H	1e3	1e4	10
s + s → H_2	1	1e10	1e10
Co-H + Co-H → A + H_2	0.001	1e6	1e9
A → Co(II) + Co(II)	117.5*	1e10	8.5e7

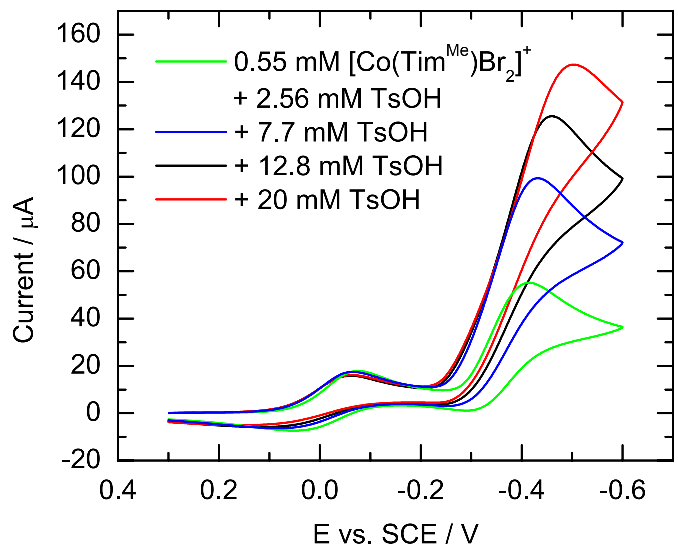
* These constants are automatically calculated by the program

Species:

	D (cm^2/s)	C (M)		D (cm^2/s)	C (M)		D (cm^2/s)	C (M)
Co(III)	2.5e-5	0	Co-H	2.5e-5	0	A	2.5e-5	0
Co(II)	2.5e-5	1.38e-4	H_2	1e-5	0			
Co(I)	2.5e-5	0	s	1e-5	0			

Acid concentrations, H^+ represents TsOH

	D (cm^2/s)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	0	2.56e-3	5.13e-3	10.2e-3



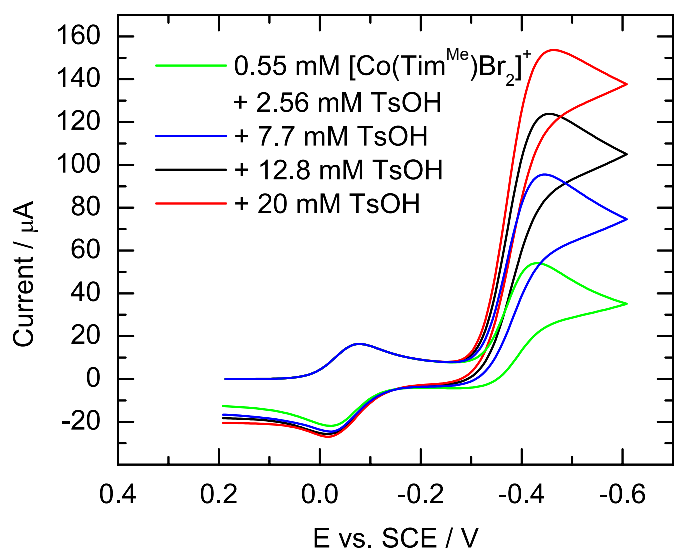


Figure S12. Experimental and simulated spectra of the catalytic waves for H_2 evolution catalysis using 0.55 mM of **4a** as the catalyst; top: experimental data; bottom: simulation using a bimetallic mechanism.

Specific Parameters for Simulation in Figure S12:

Estart (V)	Erev (V)	Eend (V)
0.2	-0.6	0.2

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + e^- → Co(II)	-0.05	0.5	10000
Co(II) + e^- → Co(II)	-0.38	0.5	10000
H^+ + e^- → s	-0.23	0.5	0

Chemical reactions:

Rxn	Keq	kf	kb*
Co(I) + H^+ → Co-H	1e3	1e4	10
s + s → H_2	1	1e10	1e10
Co-H + Co-H → A + H_2	0.001	1e6	1e9
A → Co(II) + Co(II)	117.5*	1e10	8.5e7

* These constants are automatically calculated by the program

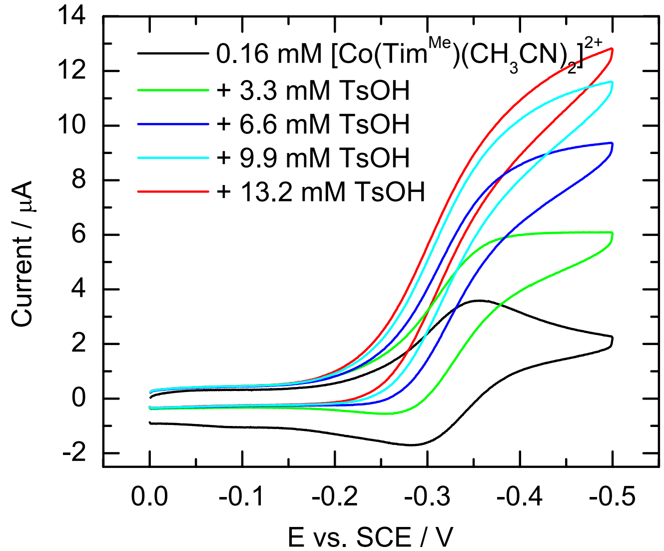
Species:

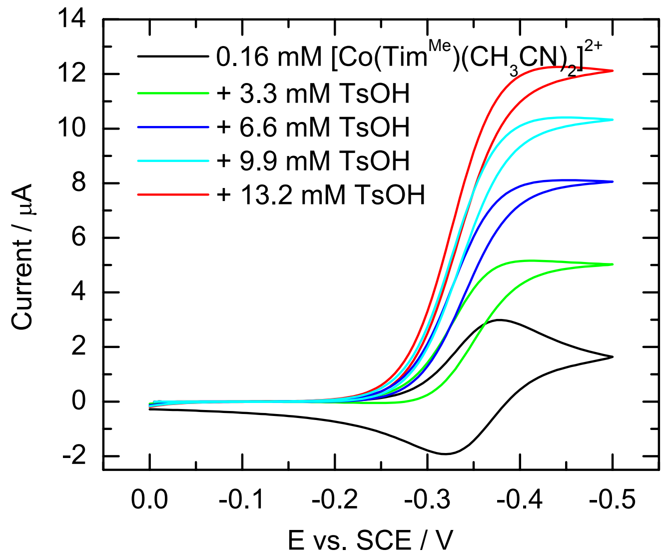
	D (cm^2/s)	C (M)		D (cm^2/s)	C (M)		D (cm^2/s)	C (M)
Co(III)	2.5e-5	0	Co-H	2.5e-5	0	A	2.5e-5	0
Co(II)	2.5e-5	5.5e-4	H_2	1e-5	0			

Co(I)	2.5e-5	0	s	1e-5	0

Acid concentrations, H^+ represents TsOH

	D (cm^2/s)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	2.56e-3	7.7e-3	12.8e-3	20e-3


0.16 mM [Co(Tim^Me)(CH3CN)2]2+
+ 3.3 mM TsOH
+ 6.6 mM TsOH
+ 9.9 mM TsOH
+ 13.2 mM TsOH
Current / μA
E vs. SCE / V


0.16 mM [Co(Tim^Me)(CH3CN)2]2+
+ 3.3 mM TsOH
+ 6.6 mM TsOH
+ 9.9 mM TsOH
+ 13.2 mM TsOH
Current / μA
E vs. SCE / V

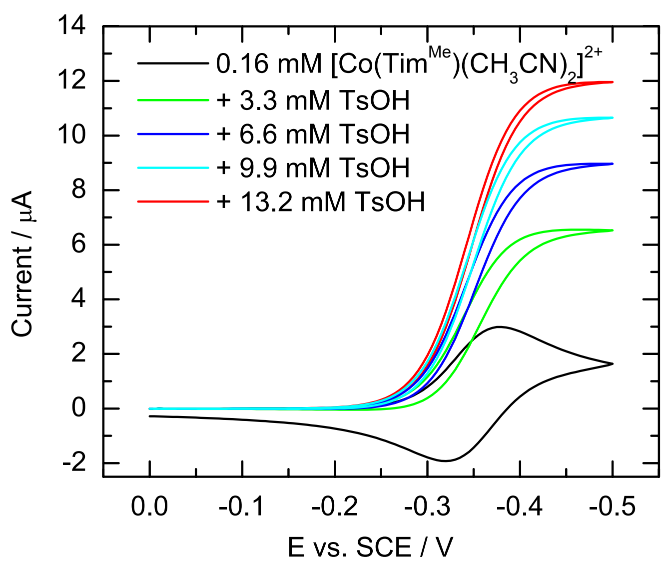

0.16 mM [Co(Tim^Me)(CH3CN)2]2+
+ 3.3 mM TsOH
+ 6.6 mM TsOH
+ 9.9 mM TsOH
+ 13.2 mM TsOH
Current / μA
E vs. SCE / V

Figure S13. Experimental and simulated spectra of the catalytic waves for H_2 evolution catalysis using 0.16 mM of **4b** as the catalyst; top: experimental data; middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, the simulations can not distinguish a monometallic mechanism from a bimetallic mechanism.

Specific Parameters for Simulation in Figure S13:

Estart (V)	Erev (V)	Eend (V)
0	-0.5	0

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + e^- → Co(II)	0.2	0.5	10000
Co(II) + e^- → Co(II)	-0.35	0.5	10000
H^+ + e^- → s	-0.23	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	Keq	kf	kb*
Co(I) + H^+ → Co-H	300	8000	26.6
s + s → H_2	1	1e10	1e10
Co-H + H^+ → Co(III) + H_2	1.9e-8	650	4e10
Co(III) + Co(I) → Co(II) + Co(II)	1.9e9*	1e10	5

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
$Co(I) + H^+ \rightarrow Co\text{-}H$	500	2e3	4
$s + s \rightarrow H_2$	1	1e10	1e10
$Co\text{-}H + Co\text{-}H \rightarrow A + H_2$	1000	3e5	300
$A \rightarrow Co(II) + Co(II)$	4.5e5*	1e10	2.2e4

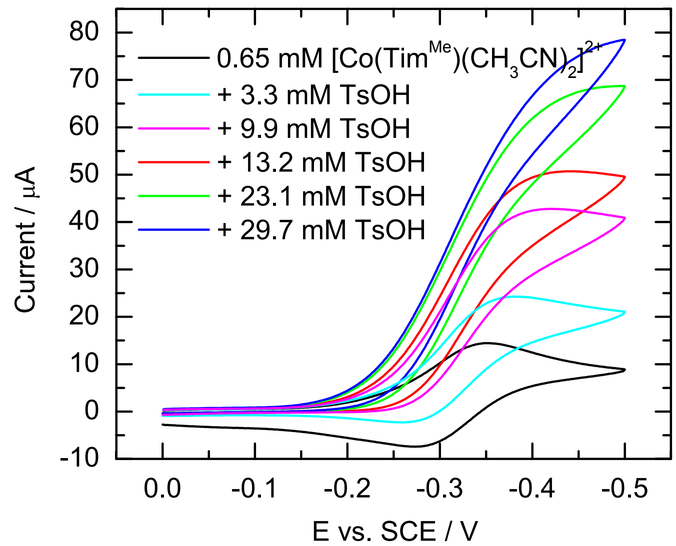
* These constants are automatically calculated by the program

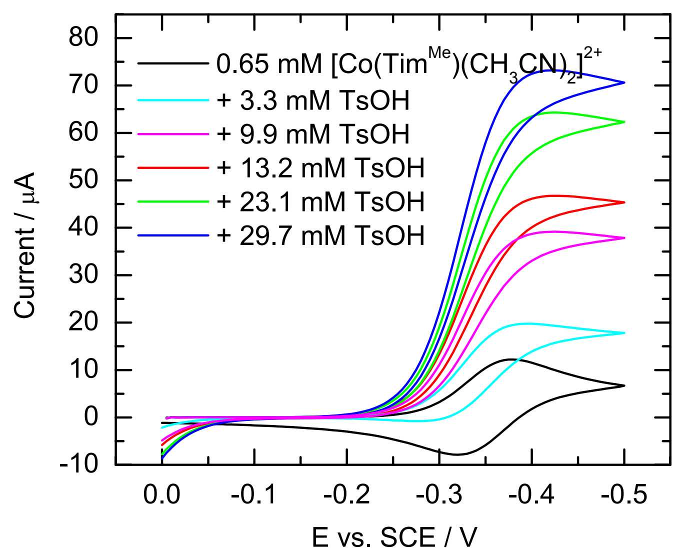
Species:

	D (cm^2/s)	C (M)		D (cm^2/s)	C (M)		D (cm^2/s)	C (M)
Co(III)	1.2e-5	0	Co-H	1.2e-5	0	A	1.2e-5	0
Co(II)	1.2e-5	1.59e-4	H_2	1e-5	0			
Co(I)	1.2e-5	0	s	1e-5	0			

Acid concentrations, H^+ represents TsOH

	D (cm^2/s)	C (M)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	0	2.8e-3	8.4e-3	16.8e-3	22.4e-3


0.65 mM $[Co(Tim^{Me})(CH_3CN)_2]^{2+}$
+ 3.3 mM TsOH
+ 9.9 mM TsOH
+ 13.2 mM TsOH
+ 23.1 mM TsOH
+ 29.7 mM TsOH
Current / µA
E vs. SCE / V


0.65 mM $[Co(Tim^{Me})(CH_3CN)_2]^{2+}$
+ 3.3 mM TsOH
+ 9.9 mM TsOH
+ 13.2 mM TsOH
+ 23.1 mM TsOH
+ 29.7 mM TsOH
Current / µA
E vs. SCE / V

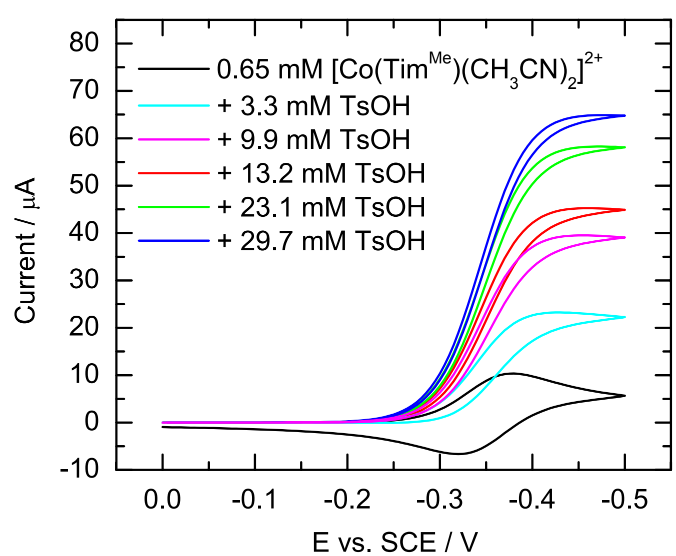

0.65 mM $[Co(Tim^{Me})(CH_3CN)_2]^{2+}$
+ 3.3 mM TsOH
+ 9.9 mM TsOH
+ 13.2 mM TsOH
+ 23.1 mM TsOH
+ 29.7 mM TsOH
Current / µA
E vs. SCE / V

Figure S14. Experimental and simulated spectra of the catalytic waves for H_2 evolution catalysis using 0.65 mM of **4b** as the catalyst; top: experimental data; middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, the simulations can not distinguish a monometallic mechanism from a bimetallic mechanism.

Specific Parameters for Simulation in Figure S14:

Estart (V)	Erev (V)	Eend (V)
0	-0.5	0

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + e^- → Co(II)	0.2	0.5	10000
Co(II) + e^- → Co(II)	-0.35	0.5	10000
H^+ + e^- → s	-0.23	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	Keq	kf	kb*
Co(I) + H^+ → Co-H	300	8000	26.6
s + s → H_2	1	1e10	1e10
Co-H + H^+ → Co(III) + H_2	1.9e-8	650	4e10
Co(III) + Co(I) → Co(II) + Co(II)	1.9e9*	1e10	5

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
$Co(I) + H^+ \rightarrow Co\text{-}H$	500	2e3	4
$s + s \rightarrow H_2$	1	1e10	1e10
$Co\text{-}H + Co\text{-}H \rightarrow A + H_2$	1000	3e5	300
$A \rightarrow Co(II) + Co(II)$	4.5e5*	1e10	2.2e4

* These constants are automatically calculated by the program

Species:

	D (cm^2/s)	C (M)		D (cm^2/s)	C (M)		D (cm^2/s)	C (M)
Co(III)	1.2e-5	0	Co-H	1.2e-5	0	A	1.2e-5	0
Co(II)	1.2e-5	1.59e-4	H_2	1e-5	0			
Co(I)	1.2e-5	0	s	1e-5	0			

Acid concentrations, H^+ represents TsOH

	D (cm^2/s)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	0	3.3e-3	9.9e-3	13.2e-3	23.1e-3	29.7e-3

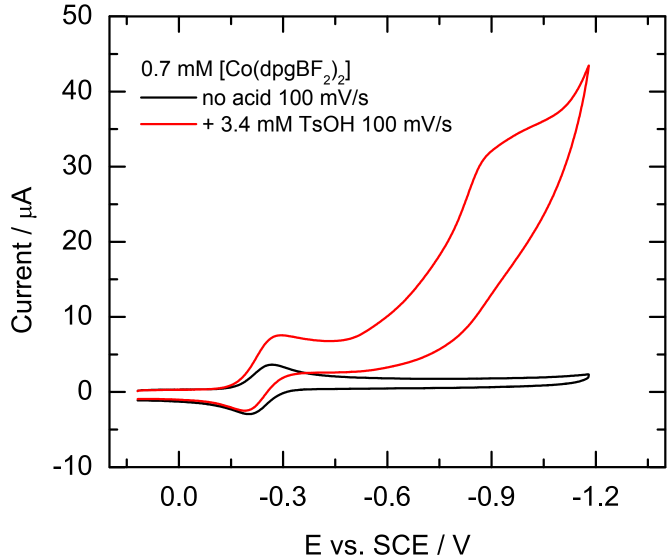


Figure S15. Cyclic voltammogram of 0.7 mM **2** in CH_3CN solution containing 0.1 M [$^nBu_4N$][ClO_4] in the absence (black) and presence (red) of 3.4 mM TsOH•H_2O showing a catalytic wave negative of the $Co^{II/I}$ potential. Scan rate: 100 mV /s^{-1}; Glassy carbon electrode.

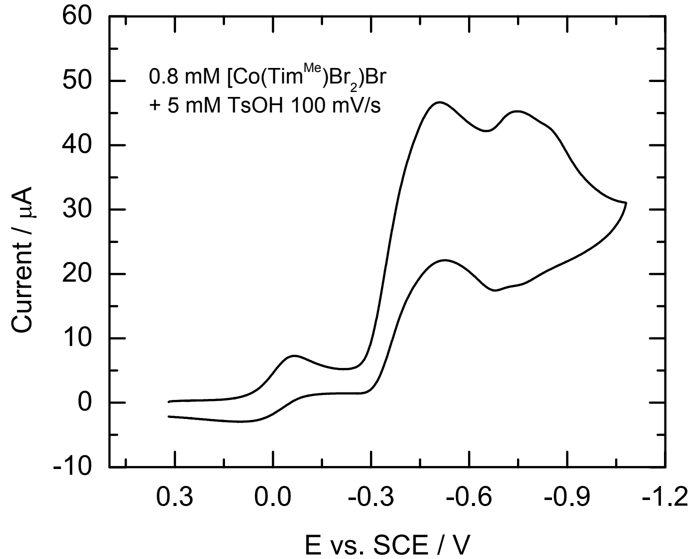
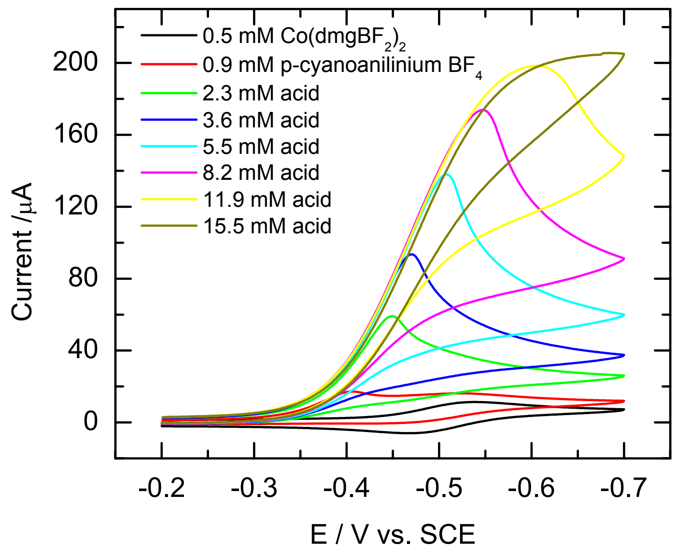
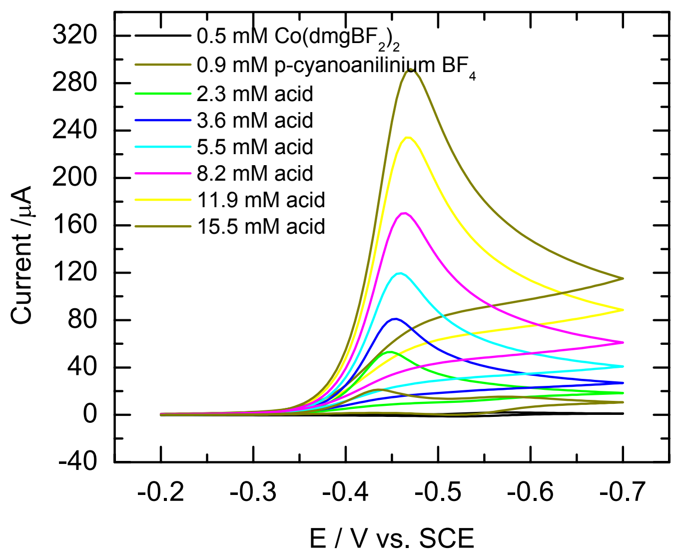


Figure S16. Cyclic voltammogram of 0.8 mM **4a** in CH_3CN solution containing 0.1 M [$^nBu_4N$][ClO_4] in presence of 5 mM TsOH•H_2O showing a redox wave negative of the $Co^{II/I}$ potential. Scan rate: 100 mV /s^{-1}; Glassy carbon electrode.


0.5 mM Co(dmgBF2)2
0.9 mM p-cyanoanilinium BF4
2.3 mM acid
3.6 mM acid
5.5 mM acid
8.2 mM acid
11.9 mM acid
15.5 mM acid
Current /μA
E / V vs. SCE


0.5 mM Co(dmgBF2)2
0.9 mM p-cyanoanilinium BF4
2.3 mM acid
3.6 mM acid
5.5 mM acid
8.2 mM acid
11.9 mM acid
15.5 mM acid
Current /μA
E / V vs. SCE

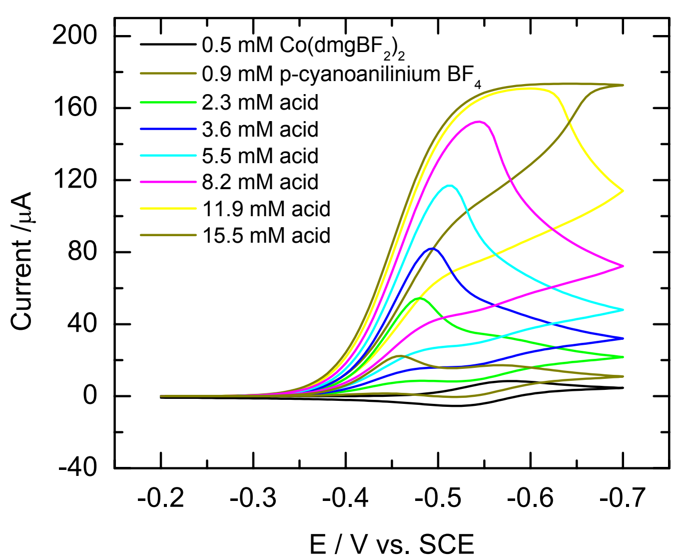

0.5 mM Co(dmgBF2)2
0.9 mM p-cyanoanilinium BF4
2.3 mM acid
3.6 mM acid
5.5 mM acid
8.2 mM acid
11.9 mM acid
15.5 mM acid
Current /μA
E / V vs. SCE

Figure S17. Experimental and simulated spectra of the catalytic waves for H_2 evolution catalysis using 0. 5 mM of **1** as the catalyst and p-cyanoanilinium BF_4 as the acid; top: experimental data; middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, only simulations assuming a bimetallic mechanism could give rise to satisfactory fits to the experimental data collected under all conditions.

Specific Parameters for Simulation in Figure S17:

Estart (V)	Erev (V)	Eend (V)
0	-0.5	0

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + e^- → Co(II)	0.2	0.5	10000
Co(II) + e^- → Co(II)	-0.35	0.5	10000
H^+ + e^- → s	-0.20	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	Keq	kf	kb*
Co(I) + H^+ → Co-H	3e5	7e7	233
s + s → H_2	1	1e10	1e10
Co-H + H^+ → Co(III) + H_2	4.7e-7	1e10	2e16
Co(III) + Co(I) → Co(II) + Co(II)	4.7e12*	1e10	0.002

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
$Co(I) + H^+ \rightarrow Co\text{-}H$	3e5	1e8	333
$s + s \rightarrow H_2$	1	1e10	1e10
$Co\text{-}H + Co\text{-}H \rightarrow A + H_2$	1	5e5	5e5
$A \rightarrow Co(II) + Co(II)$	7.5*	1e10	1.3e9

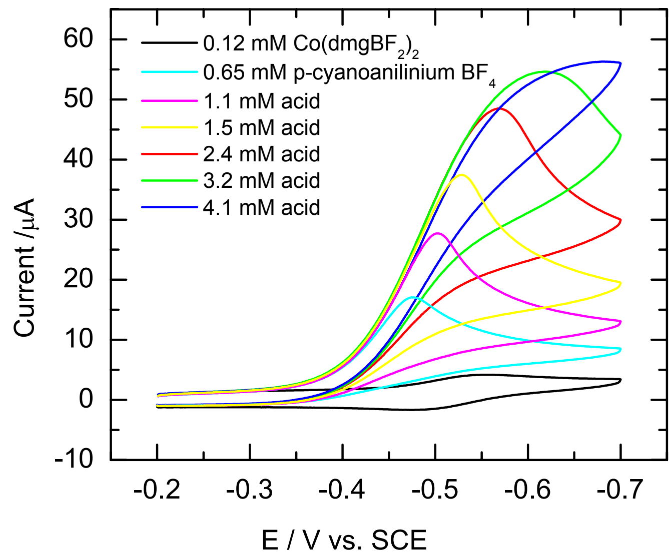
* These constants are automatically calculated by the program

Species:

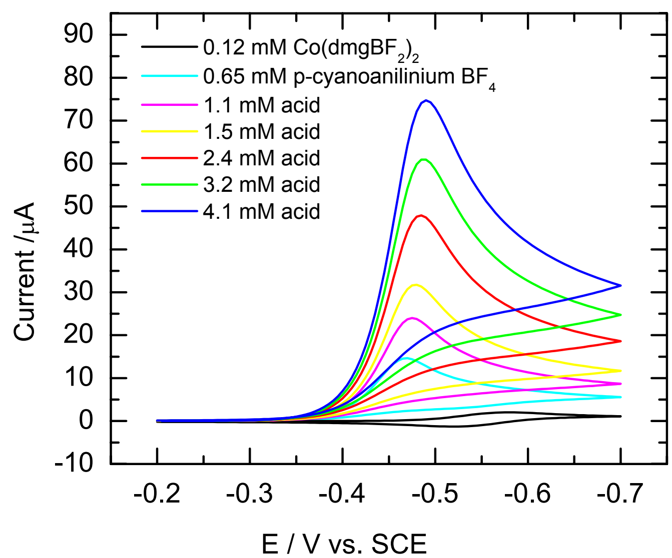
	D (cm^2/s)	C (M)		D (cm^2/s)	C (M)		D (cm^2/s)	C (M)
Co(III)	1.2e-5	0	Co-H	1.2e-5	0	A	1.2e-5	0
Co(II)	1.2e-5	5e-4	H_2	1e-5	0			
Co(I)	1.2e-5	0	s	1e-5	0			

Acid concentrations, H^+ represents p-cyanoanilinium.

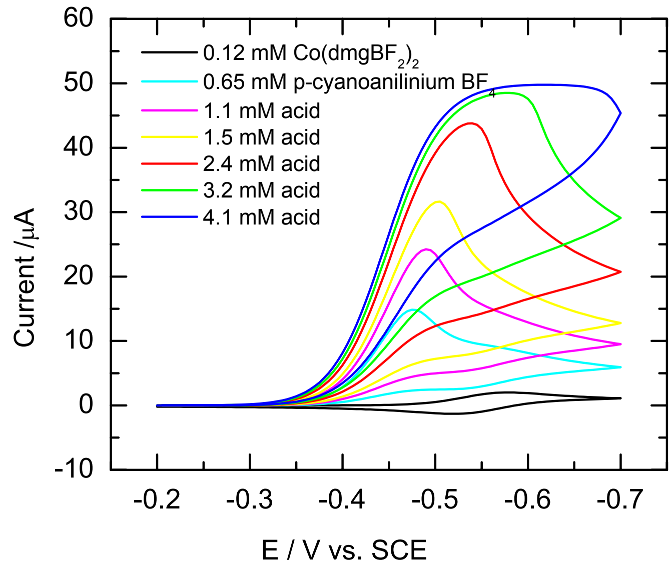
	D (cm^2/s)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	0	0.9e-3	2.3e-3	3.6e-3	5.5e-3	8.2e-3	11.9e-3	15.5e-3



0.12 mM Co(dmgBF2)2
0.65 mM p-cyanoanilinium BF4
1.1 mM acid
1.5 mM acid
2.4 mM acid
3.2 mM acid
4.1 mM acid
Current /μA
E / V vs. SCE



0.12 mM Co(dmgBF2)2
0.65 mM p-cyanoanilinium BF4
1.1 mM acid
1.5 mM acid
2.4 mM acid
3.2 mM acid
4.1 mM acid
Current /μA
E / V vs. SCE



0.12 mM Co(dmgBF2)2
0.65 mM p-cyanoanilinium BF4
1.1 mM acid
1.5 mM acid
2.4 mM acid
3.2 mM acid
4.1 mM acid
Current /μA
E / V vs. SCE

Figure S18. Experimental and simulated spectra of the catalytic waves for H_2 evolution catalysis using 0. 12 mM of **1** as the catalyst and p-cyanoanilinium BF_4 as the acid; top: experimental data; middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, only simulations assuming a bimetallic mechanism could give rise to satisfactory fits to the experimental data collected under all conditions.

Specific Parameters for Simulation in Figure S18:

Estart (V)	Erev (V)	Eend (V)
0	-0.5	0

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + e^- → Co(II)	0.2	0.5	10000
Co(II) + e^- → Co(II)	-0.35	0.5	10000
H^+ + e^- → s	-0.20	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	Keq	kf	kb*
Co(I) + H^+ → Co-H	3e5	7e7	233
s + s → H_2	1	1e10	1e10
Co-H + H^+ → Co(III) + H_2	4.7e-7	1e10	2e16
Co(III) + Co(I) → Co(II) + Co(II)	4.7e12*	1e10	0.002

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
$Co(I) + H^+ \rightarrow Co\text{-}H$	3e5	1e9	3333
$s + s \rightarrow H_2$	1	1e10	1e10
$Co\text{-}H + Co\text{-}H \rightarrow A + H_2$	1	3e6	5e5
$A \rightarrow Co(II) + Co(II)$	7.5*	1e10	1.3e9

* These constants are automatically calculated by the program

Species:

	D (cm^2/s)	C (M)		D (cm^2/s)	C (M)		D (cm^2/s)	C (M)
Co(III)	1.2e-5	0	Co-H	1.2e-5	0	A	1.2e-5	0
Co(II)	1.2e-5	1.2e-4	H_2	1e-5	0			
Co(I)	1.2e-5	0	s	1e-5	0			

Acid concentrations, H^+ represents p-cyanoanilinium.

	D (cm^2/s)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	0	0.65e-3	1.1e-3	1.5e-3	2.4e-3	3.2e-3	4.1e-3